

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B01D 61/36		A1	(11) International Publication Number: WO 93/22036 (43) International Publication Date: 11 November 1993 (11.11.93)
(21) International Application Number: PCT/AU93/00196 (22) International Filing Date: 30 April 1993 (30.04.93) (30) Priority data: PL 2190 30 April 1992 (30.04.92) AU PL 2808 5 June 1992 (05.06.92) AU		(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(71) Applicant (for all designated States except US): TYGOLA PTY.LTD. [AU/AU]; 87 Ashley Street, West Footscray, VIC 3012 (AU). (72) Inventor; and (75) Inventor/Applicant (for US only): MICHAELS, Alan, Sherman [US/US]; 210 Allandale Road, Apt. 3A, Chestnut Hill, MA 02167 (US). (74) Agent: McMaster, Wayne; Freehill Patent Services, Level 47, 101 Collins Street, Melbourne, VIC 3000 (AU).			
(54) Title: MEMBRANE EXTRACTION PROCESS			
(57) Abstract <p>The invention concerns a process for reducing the alcohol content of an aqueous mixture comprising the steps of: (a) contacting one surface of a microporous hydrophobic membrane with the aqueous mixture; (b) contacting the other surface of the membrane with water or a dilute salt solution; and (c) collecting the aqueous mixture; wherein alcohol evaporates from the aqueous mixture, passes through the membrane and is dissolved in the water or dilute brine to form an alcohol enriched liquid.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Serbia
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TC	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam

1.

MEMBRANE EXTRACTION PROCESSField of the Invention

This invention relates to a membrane extraction process for selectively removing volatile components from liquid mixtures.

5 Background of the Invention

Whilst the following description is in terms of alcohol reduction from a liquid mixture, it is to be understood that the invention is not so limited.

Alcohol reduction is at present contemplated in many industries. A major area is that of aqueous ferments such as beer and wine.

10 In the present climate, where drink-driving is strongly discouraged, and for which penalties are severe, there is great need to provide beverages which are alcohol-reduced or free of alcohol, but which taste at least very similar to alcohol-containing beverages.

15 So-called "light" beers have been developed and marketed in recent years, but to produce a palatable product, a complicated multi-stage brewing process must be used.

20 The situation with regard to "light" wines is far less developed. Those alcohol-reduced wines which have been produced have usually employed a form of distillation, resulting in the unacceptable alteration of the taste of the final product.

25 Membrane technology for separation of gaseous and liquid components is very well developed. If a multi-component fluid mixture is brought in contact with one surface of a membranous barrier - that is, a solid, homogenous film - under conditions where the other side of the membrane is in contact with another fluid, there may be a transfer of components from one fluid to the other through the membrane.

2.

A known example of alcohol extraction using a membrane has been described in a Membrana brochure titled "New process for alcoholic reduction of Beer and other Alcoholic Drinks by Means of Dialysis" by F. J. Schmitz, Membrana GmbH, Wuppertal, Germany (1983). In this process a feed stream of beer was passed over a hydrophilic membrane whereby alcohol and other components such as water and other volatiles were transported across the membrane without phase change. A reduction of alcohol content in the feed stream was reported at 6.29% vol% to 3.81 vol%. However loss of other components such as flavours and colours, Bitter units (EBC) 27 -22 and colour (EBC) 10.5 -10.0 was also reported together with loss of other organic compounds which were not derived from alcohol. Consequently such dialysis processes are not selective of one volatile component over other components in the solution and result in corresponding loss of water, flavour and colour components. Consequently the change in taste is unacceptable.

To an extent the selectivity of the extraction process for volatile components can be improved by the use of a microporous hydrophobic membrane has been described in the paper entitled "Evaporation of alcohol/water reactives through hydrophobic porous membranes" by E. Hoffman, et al; Journal of Membrane Science; 34, pp 199-206 (1987). This process discloses the evaporation of dilute solutions of methanol, ethanol, propanol in water with transport of vapour through a microporous hydrophobic porous membrane.

In this process the feed side of the membrane is maintained at atmospheric pressure whilst the pressure at the vapour phase side of the membrane is 7kPa. The vapour is enriched in alcohol only when the alcohol concentration of the feed solution is below a certain level which for ethanol/water solutions was 2% by weight. Consequently, this process is unsuitable for alcohol removal from commonly consumed alcoholic beverages such as beer (5%) and wine (12%).

It is therefore an object of this invention to provide an improved membrane extraction process for the selective extraction of a volatile component from liquid mixtures.

3.

Description of the Invention

According to one aspect of the present invention there is provided a process for selectively extracting one or more volatile components from other components in a liquid mixture comprising the steps of:

5 (a) contacting one surface of a microporous hydrophobic membrane with the liquid mixture;

(b) contacting the other surface of the membrane with a liquid in which one or more volatile components are soluble; and

10 (c) collecting the liquid mixture;

whereby the volatile component or components evaporate from the liquid mixture, pass through the membrane and are dissolved in the liquid.

No special temperature or pressure conditions need to be applied.

15 In another preferred form of the invention the liquid mixture is an aqueous solution and the volatile component is an organic compound. More preferably the liquid mixture is an aqueous solution containing alcohol as the volatile component.

20 In a preferred form of the invention the process includes the further steps of collecting the liquid and recovering the volatile component. The liquid may be recycled after the volatile component has been at least partially removed from the liquid.

One particularly preferred form is a process for reducing the alcohol content of an aqueous mixture comprising the steps of:

25 (a) contacting one surface of a microporous hydrophobic membrane with the aqueous mixture;

4.

(b) contacting the other surface of the membrane with water or a dilute aqueous saline solution; and

(c) collecting the aqueous mixture;

5 wherein alcohol evaporates from the aqueous mixture, passes through the membrane and is dissolved in the water or dilute salt solution to form an alcohol enriched liquid.

Preferred additional steps are:

(d) collecting the alcohol enriched extracting liquid;

10 (e) boiling the alcohol enriched liquid to remove the alcohol therefrom and form an alcohol depleted liquid; and

(f) recycling at least a part of alcohol depleted liquid to step (b).

15 The extracting liquid is one in which the volatile component to be extracted is highly soluble. The differences in the activity of the desired component in the two liquid phases causes a vapour pressure gradient across the membrane which provides the driving force for the transfer of that component from the liquid mixture into the extracting liquid.

20 When the liquid mixture is an aqueous solution containing alcohol, and the downstream liquid is water or an aqueous solution of a non-volatile solute the vapour pressure of alcohol at the liquid mixture side of the membrane is higher than on the other side. Consequently, the alcohol evaporates from the mixture, moves as vapour across the membrane and dissolves in the downstream liquid.

25 In another preferred form of the invention, the process comprises the further step of adjusting the concentration of solutes in the extracting liquid in order to control the absolute and relative rates of transport of

5.

water and other volatile components between the two liquids. In particular this procedure can be employed to:

- (1) remove undesirable components from the liquid mixture;
- (2) prevent loss of desirable components from the liquid mixture; or
- 5 (3) add to the liquid mixture desirable components not originally present in that solution.

Any microporous membrane the pores of which are not wetted by either liquid phase can be used for this purpose.

If the solution to be processed is aqueous, and the component to be extracted is a volatile solute such as alcohol, a preferred class of membranes which are non-wettable by water and aqueous solutions, but freely permeable to gases and vapours. Examples include microporous polytetrafluoroethylene membranes such as those sold under the trade name Goretex, or microporous polypropylene membranes such as those 15 sold under the trade marks Celgard and Accurel.

Any other microporous, non-water-wettable structure available in thin-film or hollow-fiber form, including ceramic and metallic as well as organic polymeric structures are suitable for this application. Such hydrophobic microporous membranes are particularly well suited to the process of the 20 present invention because they are highly permeable to highly volatile solutes such as alcohol, ketones, aldehydes and esters and virtually impermeable to nonvolatile solutes such as sugar or salts, and only slightly permeable to low-volatility solutes such as flavour and fragrance components present in most alcoholic beverages and ferments.

25 **EXAMPLES**

The invention will now be more fully described by reference to further examples.

6.

In the following experiments, the "feed" (or "upstream") liquid is that which contains the component to be removed, and the "downstream" liquid is that to which the volatile component is desired to be passed, through the membrane.

5. Example 1

In the first experiment, the upstream liquid selected was wine and the downstream liquid selected was an aqueous salt solution (or brine) containing 27% sodium chloride by weight. The membrane was a microporous polytetrafluoroethylene membrane sold under the trade name GoreTex. A reduction of alcohol concentration in the feed stream from about 12° to about 9° within 10 minutes was observed. Thereafter a much slower removal, (accompanied by transfer of water from the wine across the membrane), occurred, which resulted in unwanted concentration of non-volatiles in the feed stream.

15 The inability of the brine solution to further remove alcohol from the feed stream is a consequence of the fact that the vapour pressure of alcohol over a 3% solution of alcohol in the brine is actually greater than that over a 9% alcohol ferment. Moreover, the reduced vapour pressure of water over the brine relative to that over the wine resulted in the 20 (undesirable) removal of water from the ferment.

Hence, it was believed that by substituting water (or a more dilute brine) as the extracting solution, more efficient removal of alcohol, without concomitant removal of water from the ferment, could be achieved. This illustrates the potential utility of adjustment of the 25 extracting solution composition to optimize alcohol removal without significant alteration in concentration of other ferment components. Moreover, the final alcohol concentration in the processed ferment could be easily controlled by adjusting the alcohol content of the extracting solution to the desired level.

30 It was clear that if the stripping water (downstream fluid) is recycled without the alcohol being distilled off, the process slows as alcohol in the feed decreases and alcohol in the (downstream) solution increases. The

7.

process will stop when the vapour pressures of alcohol over the two fluids are equal.

Example 2

5 In a second experiment, substantially pure water was used as the downstream fluid. It was found that this arrangement produced rapid alcohol removal, without detectable concentration of non volatile solutes in the feed stream.

In this manner, it was possible to remove virtually all the alcohol from the feed.

10 It was found that the alcohol free wine produced from experiment 2 was found to have retained most of its flavour/fragrance volatiles, and accordingly the taste of the product was acceptable.

15 It is considered that the process of this invention prevents removal of those flavour/fragrance volatiles because of the combination of a high rate of alcohol removal and low processing temperature under which conditions the much less volatile flavour and fragrance components remain in the feed liquid.

Example 3

20 The invention can also be used to manipulate the concentration of any volatile component in the feed. For the purposes of this example, volatile components are divided into three categories:

- 1) the primary solvent (water in the case of wine);
- 2) the primary volatile solute (alcohol in the case of wine); and
- 25 3) secondary volatile solutes (flavours and fragrances in the case of wine).

Through manipulation of the extracting solution (stripper) composition, the fluxes (rates of transfer across the membrane) of these three categories of volatile components can be varied independently. For

8.

example, adding alcohol to the stripper will decrease the flux of alcohol from the feed to the stripper. Adding a non-volatile solute such as salt or sugar to the stripper will increase the flux of water from the feed to the stripper. Adding high concentrations of fragrances to the stripper 5 will cause a negative flux of fragrances, i.e., will cause a flow of fragrances from the stripper into the feed. Hence, by manipulating the levels of alcohol, salt and fragrances in the stripper, specified concentrations of alcohol, water and fragrance components can be achieved in the feed.

10 The manipulation of water and alcohol fluxes has been demonstrated experimentally for a GoreTex membrane with a 0.2 μm pore size. Alcohol fluxes have been measured for a range of feed concentrations up to 12% alcohol in wine. According to the relevant microporous membrane gas permeation theory, the flux of a gas or vapour is proportional to the 15 pressure difference of that gas or vapour across the membrane. The measured alcohol fluxes have been correlated by the equation $\text{Flux} = 1.6 \delta P_e$, where the flux is measured in kg of alcohol per square metre of membrane per hour ($\text{kg}/\text{m}^2\text{hr}$), and δP_e is the difference in alcohol vapour pressure across the membrane, measured in kPa. Water vapour fluxes have also been measured for the GoreTex membrane for various 20 concentrations of NaCl in the stripper solution up to 27 wt%. The measured water fluxes have been correlated by the equation $\text{Flux} = 2.0 \delta P_w$, where δP_w is the difference in water vapour pressure across the membrane. Also, alcohol fluxes from wine to a 27 wt% NaCl solution 25 have been measured. The alcohol flux decreases as the feed concentration decreases and the stripper alcohol concentration increases, and alcohol flux was found to cease when the feed contained 9% alcohol and the stripper contained 3% alcohol (in a 27 wt% NaCl solution). The presence of NaCl in the stripper in this experiment increased the alcohol activity to such an extent that the vapour pressure of alcohol over the 3% stripper solution was equal to the vapour pressure of alcohol over the 9% alcohol wine.

30

The above experimental correlations can be used to demonstrate the control of alcohol and water fluxes in the practice of the invention. The

9.

Table below shows alcohol and water fluxes from a 9% alcohol wine to various stripper solutions.

Stripper Composition (%)			Flux (kg/m ² hr)	
<u>Number</u>	<u>Alcohol</u>	<u>NaCl</u>	<u>Alcohol</u>	<u>Water</u>
5	1	0	1.0	-0.2
	2	0	1.0	0
	3	0	1.0	1.38
	4	3	0.54	-0.2
	5	3	0.40	0
10	6	3	0	1.38

The first three entries in the Table show that by having no alcohol in the stripper, and by varying the NaCl concentration in the stripper, alcohol fluxes can be kept constant, while water fluxes can be varied from -0.2 to 1.38 Entries 1 and 4, 2 and 5, and 3 and 6 show that for 15 any given NaCl composition (or any water flux), alcohol fluxes can be decreased by the addition of alcohol to the stripper solution. In a similar fashion, the flux of any volatile component can be manipulated by adjusting its concentration in the stripper solution.

10.

CLAIMS

1. A process for selectively extracting one or more volatile components from other components in a liquid mixture comprising the steps of:-
 - 5 (a) contacting one surface of a microporous hydrophobic membrane with the liquid mixture;
 - (b) contacting the other surface of the membrane with an extracting liquid in which one or more volatile components is soluble; and
 - (c) collecting the liquid mixture;

10 whereby the volatile component or components evaporate from the liquid mixture, passes through the membrane and are dissolved in the liquid.

- 2. A process according to claim 1 comprising the further steps of collecting the extracting liquid, and recovering the volatile component.
- 15 3. A process according to claim 2 comprising the further step of recycling the liquid after the volatile component has been at least partially recovered from the extracting liquid.
- 4. A process according to either claim 1 or 2 wherein the liquid mixture is an aqueous solution.
- 20 5. A process according to any one of claims 1 to 3 wherein, the extracting liquid is an aqueous solution of a non-volatile solute.
- 6. A process according to any one of claims 1 to 4 wherein the extracting liquid is water.
- 25 7. A process according to any one of claims 1 to 5 wherein the extracting liquid is an aqueous solution of a non-volatile solute.

11.

8. A process according to claim 7 wherein the solute is a water soluble salt liquid is a dilute brine.
9. A process according to claim 7 wherein the solute is a sugar.
10. A process according to any one of claims 1 to 7 wherein the volatile component is an organic compound.
11. A process according to any one of claims 1 to 8 wherein the liquid mixture is an aqueous solution containing alcohol.
12. A process according to any one of claims 1 to 9 comprising the further step of adjusting the concentration of solutes in the extracting liquid to control evaporation and passage of volatiles or water across the membrane.
13. A process for reducing the alcohol content of an aqueous mixture comprising the steps of:
 - (a) contacting one surface of a microporous hydrophobic membrane with the aqueous mixture;
 - (b) contacting the other surface of the membrane with water or a dilute aqueous salt solution; and
 - (c) collecting the aqueous mixture;wherein alcohol evaporates from the aqueous mixture, passes through the membrane and is dissolved in the water or dilute salt solution to form an alcohol enriched liquid.
14. A process according to claim 11 comprising the further steps of:
 - (d) collecting the alcohol enriched extracting liquid;
 - (e) boiling the alcohol enriched liquid to strip the alcohol therefrom and form an alcohol depleted liquid; and

12.

(f) recycling at least a part of alcohol depleted liquid to step (b).

15. A process according to either claims 10 or 11 comprising the further step of adjusting the concentration of solutes in the water or dilute salt solution to control evaporation and passage of volatiles or water across the membrane.

5

16. A process according to any one of claims substantially as hereinbefore described by reference to the examples.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 93/00196

A. CLASSIFICATION OF SUBJECT MATTER
Int. CL⁵ B01D 61/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC B01D 61/36Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	WO,A, 87/02380 (SEPRACOR. INC.) 23 April 1987 (23.04.87) See whole document.	(1-16)
X	Derwent Abstracts Accession No. 91-153732/21 D16, Class JO1, JP,A, 03-089922 (CHOKAN K) 15 April 1991 (15.04.91)	(1,4-7,11,13)
A	US,A, 4952751 (BLUME et al) 28 August 1990 (28.08.90)	
A	AU,B, 33543/68 (427284) (VARTA AKTIENGESELLSCHAFT) 21 August 1969 (21.08.69)	

Further documents are listed
in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :
 "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search
10 August 1993 (10.08.93)

Date of mailing of the international search report

18 AUG 1993 (18.08.93)

Name and mailing address of the ISA/AU

Authorized officer

AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
PO BOX 200
WODEN ACT 2606
AUSTRALIA*L. O. + 3. 1. Kazz-wan...*

Facsimile No. 06 2853929

D. DIAS-ABEY

Telephone No. (06) 2832136

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 93/00196

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	WO,A, 88/05768 (EXON CHEMICAL PATENTS INC.) 11 August 1988 (11.08.88)	
A	Derwent Abstract Accession No. 86-275482/42 A88E19 Class JO1, JP,A, 61-200814 (AGENCY OF IND SU TECH 5 September 1986 (05.09.86)	